New Amine-containing Polymers: Thermally Responsive Macromolecules and Matrices for Silica-based Composite Materials

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Our work has been initiated from the study of substances taking part in formation of the siliceous constructions in living organisms. Investigation of organic compounds associated with siliceous frustules of diatom algae had resulted in discovering of methylated oligopropylamines [1] which physiological function is not clear yet. We have elaborated a step-wise approach to synthetic analogues of methylated oligopropylamines [2]. The availability of oligopropylamines allowed us to synthesize more complicated compounds, including acrylate monomers [3]. The other way to amine-containing polymers consists in the reaction of poly (acryloyl chloride) or poly (methacryloyl chloride) with oligopropylamines containing one primary or secondary amine group.

The obtained polymeric derivatives of N,N-diethyl-N'-methylpropane-1,3-diamine show microphase separation (cloud point) at 40-90 ^{o}C depending on pH and composition. Dynamic light scattering data point to aggregation of the macromolecules in water solution at elevated temperatures near cloud point and also at low pH values (7-9) which give rise to unusual 1-3 micrometer size particles. According to potentiometry data, basicity of the polymers decrease with temperature increase which points on participation of ionic/hydrogen bonds between amine groups in the macromolecular compaction at elevated temperatures. The reaction of poly (acryloyl chloride) with the lack of amine gives rise to polymeric ampholytes of various isoelectric points.

Condensation of silicic acid (produced from sodium hydroxide) in the presence of polymeric propylamines results in composite precipitates which consist of spherical submicrometer particles. Calcination of these precipitates at 550 ^{o}C do not change the particles shape and gives rise to siliceous material with high surface area (500-600 m^2/g). In the case of polyampholyte copolymers, the large particles consist of small (<50 nm) nanoparticles which form a porous structure. Slow influx of silicic acid into solution of thermally responsive polymer near cloud point was realized using two-phase system with tetramethoxysilane in chloroform. This resulted in $Si(OH)_4$ condensation around large polymeric aggregates with formation of hollow ellipsoid-like particles. Physiology and technology aspects of the amino-containing polymer - silicic acid interaction will be discussed too.

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